

1.127.338



1.127.338

Date of Application and filing Complete Specification: 15 June, 1967.
No. 27644/67.

Application made in United States of America (No. 637905) on 12 May, 1967.
(Patent of Addition to No. 1117629 dated 14 Dec., 1965.)

Complete Specification Published: 18 Sept., 1968.

© Crown Copyright 1968.

DE 1618795

Index at acceptance: —C2 C2B56

Int. Cl.: —C 07 c 119/04

COMPLETE SPECIFICATION

4,4'-Methylene Bis(Cyclohexyl Isocyanate) Isomers

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, located at
5 Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
10 The present invention concerns improvements in and relating to 4,4'-methylene bis (cyclohexyl isocyanate), and is an improvement in or modification of the invention of Application No. 27643/67 (Serial No. 1,117,629).

It has long been recognized as having been very desirable that some commercial materials, especially diisocyanates, should be
20 available in liquid form under normal atmospheric conditions of temperature and pressure, since this enables an operator to handle them by means of pumping devices without any necessity to provide heated storage facilities and pumping lines, which are expensive and inconvenient, and often lead to deterioration, e.g. discoloration, of the heated materials and/or of their reaction products. In spite
25 of the fact that this has long been recognized, there has not so far been available commercially a normally liquid form of 4,4'-methylene bis (cyclohexyl isocyanate).

Diisocyanates are well-known commercial materials, being made generally by phosgenation of the corresponding diamine, and being
35 used principally for the preparation of polyurethane derivatives by reaction of the isocyanato groups with the hydroxy groups of a polyether or polyester, and/or the preparation of polyurea derivatives by reaction of the isocyanato groups with water or diamines. 4,4'-methylene bis (cyclohexyl isocyanate) is a known aliphatic solid compound and may be

prepared by conventional phosgenation of 4,4'-methylene bis (cyclohexylamine), e.g. by a phosgenation process of the type disclosed in Beck U.S. Specification No. 2,822,373. 4,4'-methylene bis (cyclohexylamine) itself can exist in three stereoisomeric forms, referred to as the cis-cis, the trans-trans and the cis-trans isomers, as set out in detail in Whitman U.S. Specification No. 2,606,925 and U.S. Specifications Nos. 2,494,563 (Kirk, et al), 2,606,924 (Whitman), 3,153,088 and 3,155,724 (Arthur) all disclose various combinations of these 4,4'-methylene bis (cyclohexylamine) isomers and processes for obtaining desired isomers and combinations thereof.

There is now provided, according to the present invention, a mixture of 4,4'-methylene bis (cyclohexyl isocyanate) isomers that is liquid at 30°C. or preferably even at 25°C. or even lower, such as 20°C. Such normally liquid mixtures generally contain, by weight, less than 26% of the trans-trans isomer, preferably less than 23%, and less than 75% of the cis-cis isomer, preferably less than 72%. The m.p. of the cis-trans isomer is 17—18°C.

These normally liquid mixtures having the desired proportions of 4,4'-methylene bis (cyclohexyl isocyanate) isomers may be prepared by conventional phosgenation of the respective 4,4'-methylene bis (cyclohexylamine) isomers, or by preparing pure 4,4'-methylene bis (cyclohexyl isocyanate) isomers and mixing the isomers together in appropriate proportions, or by preparing normally solid mixtures of such isomers and then adjusting the proportions of the isomers in such mixtures by conventional techniques, such as adding or extracting some of any desired or undesired isomer until the mixture is normally liquid as required.

The principal expected use of the new

materials of the present invention is as convenient starting material for the preparation of polyurethanes and/or polyureas, and it will be understood that minor amounts of phosgenation by-products and impurities may be tolerated sometimes for such purposes, e.g. these in crude or undistilled mixtures of 4,4'-methylene bis (cyclohexyl isocyanate) isomers obtained by phosgenation processes, and including any material such as 2,4'-di (isocyanatocyclohexyl) methane obtained by phosgenating the small amount of the corresponding diamine that may be present in the diamine mixture subjected to phosgenation.

Our copending Application No. 27643/67 (Serial No. 1,117,629) concerns a mixture of 4,4'-methylene bis (cyclohexyl isocyanate) isomers comprising, by weight, 15—17% of trans-trans isomer, 4% cis-cis isomer and 76% cis-trans isomer, the remaining 4% being 2,4'-di (isocyanato cyclohexyl) methane.

The invention is further illustrated in the following Examples; all parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

77 parts/hour of a mixture of 4,4'-methylene bis (cyclohexylamine) isomers containing 19% trans-trans isomer, 14% cis-cis isomer, 62% cis-trans isomer and 5% 2,4'-di (amino cyclohexyl) methane are phosgenated substantially according to the Beck process (U.S. 2,822,373) in 13% solution of o-dichlorobenzene, using 14.1 parts/hr. (50% excess) of phosgene in 7% solution in o-dichlorobenzene, the temperature being maintained at 165°C. in the reservoir and loop and the pressure being 5 psig in the reservoir and 20 psig in the loop; the average residence time is 2 hours, material being recirculated through the loop at about 650 parts/min. The product, still at 165°C., is contacted with 10 parts/hr. of phosgene at 20 psig for 30 minutes in a stirred vessel and then distilled to remove low boiling materials and o-dichlorobenzene. The conversion to product 4,4'-methylene bis (cyclohexyl isocyanate) is about 96% of theory. The crude product is distilled in a vertical wiped film molecular still at a film pressure of 200—250 microns Hg and an outside wall temperature of 155—165°C. to give 4,4'-methylene bis (cyclohexyl isocyanate) of m.p.

about 21°C. and purity greater than 99%, based on isocyanate content.

EXAMPLE 2

Substantially pure isomers of 4,4'-methylene bis(cyclohexyl isocyanate) are prepared and mixed together in the following proportions to give mixtures having an m.p. indicated in the Table. The mixtures are all cooled to below -20°C. until they crystallize and are then allowed to stand at 25°C., whereupon they all liquefy completely.

Sample	trans-trans%	cis-trans%	cis-cis%
A	20	80	—
B	22	61	17
C	20	40	40
D	15	30	55
E	—	30	70
F	15	15	70

Application No. 27643/67 (Patent No. 1,117,629) claims a mixture of 4,4'-methylene bis (cyclohexyl isocyanate) isomers, containing, by weight 15—17% of the trans-trans isomer, 4% of the cis-cis isomer and 76% of the cis-trans isomer, and no claim to the said mixture as claimed in Application No. 27643/67 (Serial No. 1,117,629) is made herein.

SUBJECT TO THE FOREGOING DISCLAIMER WHAT WE CLAIM IS:—

1. A mixture of 4,4'-methylene bis (cyclohexyl isocyanate) isomers that is liquid at 30°C.
2. A mixture according to Claim 1, that is liquid at 25°C.
3. A mixture according to Claim 1 or 2, comprising, by weight, less than 23% of the trans-trans isomer and less than 72% of the cis-cis isomer.
4. A mixture according to any of Claims 1 to 3, substantially as hereinbefore described.
5. Any of the mixtures according to Claim 4, substantially as described in either of the foregoing Examples.

For the Applicants:
FRANK B. DEHN & CO.,
Chartered Patent Agents,
Imperial House, 15—19, Kingsway,
London, W.C.2.